

Control Volume Thermodynamics (CVT) Package Reference Manual

The Control Volume Thermodynamics (CVT) package in the MELCOR code handles thermodynamic calculations for the control volumes included in a MELCOR calculation. Together with the Control Volume Hydrodynamics (CVH) and Flow (FL) packages, it is used to advance the description of the thermal/hydraulic state in the control volumes from one time level to the next. It obtains the properties of the materials which occupy these volumes from the NonCondensable Gas (NCG) and Water (H2O) packages. Details may be found in the Reference Manual for this package. This Reference Manual describes the assumptions, models, and solution strategies used in the various subroutines which make up the CVT package. Because there is no user input for this package, there is no Users' Guide for it.

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1. Introduction

MELCOR's Control Volume Thermodynamics (CVT) package calculates the thermodynamic state of the materials in each control volume from the total volume, the energies, and the masses calculated by the Control Volume Hydrodynamics (CVH) package. The contents of the control volume may be divided into a *pool* containing water which may be subcooled (liquid) or saturated (two-phase), and an *atmosphere* containing water vapor, liquid water *fog*, and noncondensable gases (NCGs). While the terms "pool" and "atmosphere" suggest a quiescent, stratified configuration, the modeling in CVT assumes only that the two components occupy disjoint subvolumes of the total control volume. (Modeling in other areas of MELCOR, however, often assumes stratification.)

In addition to familiar thermodynamic properties such as pressure, heat capacity, and compressibility, the CVT package also calculates the derivatives of the pressure in the volume with respect to its energy and mass contents for use by the implicit flow solver in the CVH package.

Two thermodynamic options are available: equilibrium and nonequilibrium. In MELCOR, equilibrium thermodynamics assumes that the pool and the atmosphere are in thermal and mechanical equilibrium, i.e., that they have the same temperatures and pressures. This implies instantaneous energy and mass transfers between pool and atmosphere.

When the equilibrium option is used, the distinction between pool and atmosphere does not affect the thermodynamics. CVT uses the total mass and energy contents of the control volume to determine its pressure and temperature. All NCGs are assumed to reside in the atmosphere; the assignment of water to pool or atmosphere is made using time-dependent information from the CVH package. Under current modeling, no water vapor is assigned to the pool, but liquid water may be assigned to the atmosphere as *fog*.

Nonequilibrium thermodynamics, on the other hand, assumes mechanical equilibrium but not thermal equilibrium, so that pressures are equal but temperatures may be different. Complete equilibrium is assumed to exist within the subvolume occupied by the pool and within that occupied by the atmosphere, making this a more limited definition of nonequilibrium than is used in some other codes. The pool may contain water vapor, called *void*, and the atmosphere may contain *fog*. Energy and mass transfers between pool and atmosphere resulting from convection/conduction, radiation, and boiling are explicitly calculated in the CVH package. The elimination of void is also computed in the CVH package, using a bubble rise model. The precipitation of fog is treated by the RadioNuclide package (if it is active) and by the CVH package. The volume (PdV) work done by the pool on the atmosphere (or vice versa) must also be accounted for; this is handled in the CVT package itself.

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When the nonequilibrium option is used, the thermodynamic state is calculated based on the mass and the total energy of the pool, the masses of the individual components of the atmosphere and their total energy as defined by CVH, and the total volume available to be shared by pool and atmosphere. Part of CVT's job is to determine the partition of the total volume between the pool and the atmosphere such that the pressures of each are equal. Each subvolume is treated as adiabatic in this calculation; thus PdV work is accounted for within the CVT package but heat and mass transfer are not. Because the pool and the atmosphere are each in internal equilibrium, the nonequilibrium option requires application of the equilibrium assumptions within each subvolume.

The CVT package consists of various interfaces to a mixed-material (water and noncondensable gases) equation of state. Properties for water and for noncondensable gases are obtained from the H2O and NCG packages, respectively. An important feature of the formulation is that it is analytic as well as thermodynamically consistent. Therefore, in contrast to equations of state based on tables or independent polynomial fits, all calculated properties are consistent (for example, a small change in mass or energy produces a change in pressure that agrees to several significant figures with that estimated from the derivatives). The structure of CVT modeling is illustrated in Figure 1.1. The block in the figure labeled "subvolume" implements the mixed-material equation of state in MELCOR as described in Section 2; its use in the nonequilibrium model is described in Section 3.

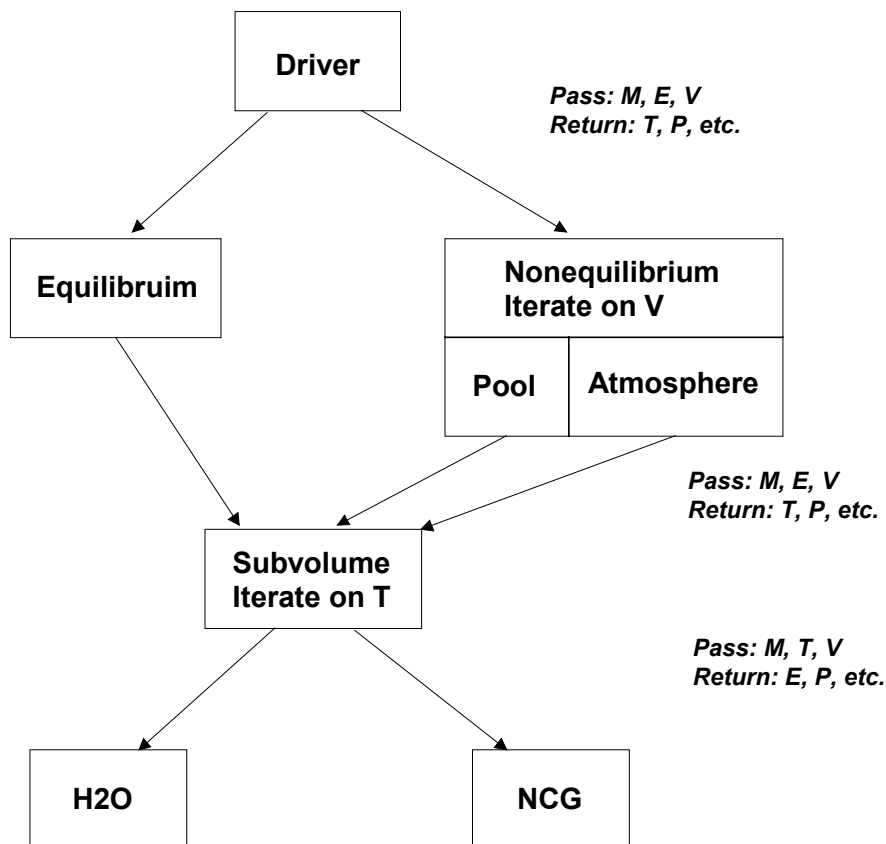


Figure 1.1 CVT model structure.

2. Equilibrium Thermodynamics

Central to all thermodynamics in MELCOR is a mixed-material equilibrium equation of state that determines all thermodynamic properties of mixtures of water and noncondensable gases. This equation of state is applied directly to MELCOR control volumes for which the option of equilibrium thermodynamics has been specified. For volumes where nonequilibrium thermodynamics is specified, it is applied separately to the atmosphere and to the pool. In the latter case, it reduces to the equation of state for water, because NCGs are not currently permitted in the pool.

The remainder of this section describes the mixed-material equation of state, in the context of its application to an equilibrium volume. The application to a nonequilibrium volume is described in Section 3.

2.1 Governing Assumptions

Equilibrium thermodynamics assumes that the pool and atmosphere temperatures are identical. Given the total volume, the total internal energy, and the masses of water and NCGs, the problem is to calculate the temperature, the total pressure, the partial pressures of each material, and various other thermodynamic properties. Because all temperatures are assumed equal and surface tension effects are not modeled, the distinction between liquid water as fog or in the pool is immaterial within equilibrium thermodynamics, as is the distinction between water vapor in the atmosphere or in a saturated pool. The assignment of liquid and vapor water to the different possible locations is made after the equilibrium state is determined, using time-dependent information from the CVH package. Therefore, within this section, *pool* will be used to mean “liquid water” and *atmosphere* to mean “water vapor plus NCGs.” In defining the pressure, there are three basic cases:

- (1) If no atmosphere is present (which can only occur if there is no NCG), the pressure is that of the pool.
- (2) If no pool is present, the NCGs occupy the total volume together with the water vapor; the total pressure is the sum of their partial pressures.
- (3) If both pool and atmosphere are present, their pressures as well as their temperatures are equal, and the partial pressure of water in the atmosphere is the saturation pressure for that temperature. If the atmosphere contains NCG, the pool must be subcooled (its pressure is equal to the sum of the saturation pressure and the partial pressures of the NCGs), and its density is therefore greater than saturation density. Thus, the volume of the atmosphere is greater than that which would be occupied by water vapor in the absence of NCGs. As will be noted below, certain linearizations of the equation of state of water will be used to simplify this calculation.

2.2 Governing Equations

The equilibrium state for a mixture of water and NCGs in a volume, under the assumptions that the NCGs are insoluble in liquid water and form an ideal mixture with water vapor, is given by the simultaneous solution of the equations

$$\rho_\ell = \frac{M_\ell}{V_\ell} \quad , \quad (2.1)$$

$$\rho_v = \frac{M_v}{V_v} \quad , \quad (2.2)$$

$$M_\ell + M_v = M_w \quad , \quad (2.3)$$

$$V_\ell + V_v = V \quad , \quad (2.4)$$

$$g_\ell(\rho_\ell, T) = g_v(\rho_v, T) \quad , \quad (2.5)$$

$$E = M_\ell e_\ell(\rho_\ell, T) + M_v e_v(\rho_v, T) + \sum_{i=4}^N M_i e_i(T) \quad , \quad (2.6)$$

$$P = P_\ell(\rho_\ell, T) = P_v(\rho_v, T) + \sum_{i=4}^N \frac{M_i R_i T}{V_v} \quad , \quad (2.7)$$

where

ρ	is density,
M	is mass,
V	is volume,
g	is Gibbs free energy,
T	is the temperature,
E	is the total internal energy,
e	is specific internal energy,
P	is pressure,
R	is gas constant,

and the subscripts w , ℓ , v , and i refer to water, liquid water, water vapor, and the i^{th} NCG, respectively. (Within MELCOR, $4 \leq i \leq N$ for NCG, where N is the total number of *materials* in the problem.) If the Gibbs free energy, g , is considered a function of its natural variables (P, T) rather than of (ρ, T) , then g_ℓ and g_v are evaluated at $P_\ell(\rho_\ell, T)$ and $P_v(\rho_v, T)$, respectively. (It is helpful to keep in mind that when these equations are applied in MELCOR, it is the masses, the volume, and the total internal energy which are known, so that densities are more natural variables than are pressures. The temperature, which

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must actually be determined from densities and energy contents, will continue to be thought of as an independent variable in most cases.)

If water is present, but not NCGs, these relations define the equation of state for water (as calculated in the H2O package), which may exist as liquid, as vapor, or as a two-phase mixture. Equations (2.5) and (2.7), expressing equality of the chemical potentials and of the pressures of the two phases, respectively, require that the phases coexist at temperature T only at the saturation pressure $P_{sat}^o(T)$, with densities $\rho_{\ell,sat}^o(T)$ and $\rho_{v,sat}^o(T)$, where the superscript “ o ” denotes “in the absence of NCGs.”

In the presence of NCGs, the conditions for equilibrium between liquid water and water vapor are modified. The principal effect, that the pressure in the liquid must be the total pressure, is expressed in Equation (2.7). In addition, the partial pressure of water vapor at equilibrium is slightly modified by the presence of NCGs. However, this change and most of its consequences are negligibly small for the temperature and pressure ranges of interest in MELCOR, as will be shown below.

If Equation (2.5) is expanded at fixed temperature about the equilibrium state for pure water, using $dg = v dP - s dT$, and noting that $g_{\ell}(\rho_{\ell,sat}^o, T) = g_v(\rho_{v,sat}^o, T)$, the result is

$$\frac{P_{\ell}(\rho_{\ell,sat}, T) - P_{sat}^o(T)}{\rho_{\ell,sat}^o} = \frac{P_v(\rho_{v,sat}, T) - P_{sat}^o(T)}{\rho_{v,sat}^o} \quad (2.8)$$

Comparison with Equation (2.7) shows that the pressure of water vapor is increased by roughly $\rho_{v,sat}^o / \rho_{\ell,sat}^o$ times the contribution of NCGs to the total pressure. This is a quite small correction under conditions of interest, because the ratio $\rho_{v,sat}^o / \rho_{\ell,sat}^o$ is very small unless the pressure of water vapor is near the critical pressure. Even near the critical point of water, the pressure of the NCGs must be at least comparable to that of the water for the effect to be large. Problems in which such high (supercritical) pressures occur are outside the intended range of application of MELCOR. (Furthermore, if both water and NCG pressures are large, the assumption of ideality used to derive the correction is clearly in error and the correction calculated would be invalid.) Therefore, we neglect the difference between $\rho_{v,sat}$ and $\rho_{v,sat}^o$, and between $P_{sat}(T)$ and $P_{sat}^o(T)$. Because the change in saturation vapor pressure is neglected, all water vapor in equilibrium with liquid is treated as having *unmodified* saturation properties.

The presence of NCGs increases the pressure—and therefore the density—of the liquid compared to a state at the same temperature in the absence of NCGs. Although the resulting difference between $e(\rho_{\ell,sat}, T)$ and $e(\rho_{\ell,sat}^o, T)$ could be calculated, examination of steam tables (such as Keenan and Keyes) shows the difference to be comparable to the effect of a temperature change of only a fraction of a Kelvin for NCG pressures less than

100 MPa. In the interest of simplicity, this difference is neglected. However, the difference in the enthalpy, $h = e + P/\rho$, of the two states is significantly greater, and the difference between h and e is responsible for flow work done in the CVH package. Therefore, a first-order correction is made using $dh = dP/\rho$, and the enthalpy of liquid at pressure P in equilibrium with water vapor is taken as

$$h_{\ell, sat}(P, T) = h(\rho_{\ell, sat}^o, T) + \frac{P - P_{sat}(T)}{\rho_{\ell, sat}^o} \quad (2.9)$$

The most important effect of the compression of liquid water by the partial pressure of NCGs is the resulting increase in the volume available to the NCGs. This is included in detail in the model. (To understand its importance, consider the case where there would be no water vapor in the volume in the absence of NCGs. If the compression were ignored, there would be no volume available to the NCGs, and their pressure would be infinite.)

The compression also increases the volume available to water vapor and, because the density of the water vapor continues to be $\rho_{v, sat}^o$ under the present assumptions, the presence of NCGs acts to increase the mass of water vapor for a given temperature. In the extreme case where the water would be subcooled in the absence of NCGs (and there would be *no* water vapor in the volume), the NCGs will occupy a volume from which liquid water is excluded, and which therefore will contain water vapor. The associated change in the amount of each water phase is treated very simply as a small correction after the primary calculation has been completed. Any implications for the energy content of the mixture at a given temperature are ignored.

Under the approximations described above, the need for consideration of Equation (2.5) is eliminated, and Equation (2.6) may be replaced by

$$E = M_w e_w(\rho_w, T) + \sum_{i=4}^N M_i e_i(T) \quad (2.10)$$

$$\rho_w = \frac{M_w}{V} \quad (2.11)$$

involving only the normal thermal equation of state for water in terms of its bulk density. Because the energy of the NCGs does not depend on their volume, Equation (2.10) may be solved for T without the volume available to NCGs being known. This is done iteratively, with repeated calls to the water and NCG equations of state. Newton's method is used, with a secant (and ultimately a bisection) backup. When the iteration has converged, there are several cases to be considered:

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- (1) If there are no NCGs in the volume, the solution is essentially complete at this point as the water equation of state returns mixed-phase properties when appropriate. The total pressure is that returned by the equation of state for water,

$$P_{tot} = P_w(\rho_w, T) \quad (\text{no NCG}) \quad (2.12)$$

- (2) If there is no liquid water in the volume, the entire volume is available to the NCG, and the total pressure is given by

$$P_{tot} = P_w(\rho_w, T) + \sum_{i=4}^N \frac{M_i R_i T}{V} \quad (\text{no liquid}) \quad (2.13)$$

(from Equation (2.7)), which assumes that water vapor and NCG form an ideal mixture.

- (3) Otherwise, the volume contains both liquid water and NCGs. (Note that if the water occupied the volume alone at the same temperature, the state might be either two-phase or subcooled.) As suggested by the discussion above, we will treat the effects of NCGs on the properties of water as a relatively small perturbation. In the absence of NCGs, the mass balance

$$V_\ell \rho_{\ell, sat} + V_v \rho_{v, sat} = M_w \quad (2.14)$$

may be used to show that a volume

$$V_v = \min \left\{ V, \max \left[0, \frac{V \rho_{\ell, sat}(T) - M_w}{\rho_{\ell, sat}(T) - \rho_{v, sat}(T)} \right] \right\} \quad (2.15)$$

would be occupied by water vapor, and the remaining volume

$$V_\ell = V - V_v \quad (2.16)$$

would be occupied by liquid, where $\rho_{\ell, sat}(T)$ and $\rho_{v, sat}(T)$ are the densities of saturated liquid and vapor at the temperature T . (The coding contains a modification to the water phase boundary to maintain a continuous definition of “liquid” and “vapor” at high pressures and supercritical temperatures; while water should never reach such a state in a reactor, this region of the equation of state may be encountered during iterations within the code.)

The requirement that pool and atmosphere have the same pressure when NCGs are included is imposed by assuming: (1) that the presence of the NCGs causes a reduction of the volume of the liquid by δV ; (2) that the NCGs then occupy the new volume V_n , where

$$V_n = V_v + \delta V; \quad (2.17)$$

and (3) that the resulting pressure is given by the linearization of Equation (2.7) as

$$P_{tot} = \begin{cases} P_w(\rho_w, T) + \frac{\delta V}{KV_\ell} & (\text{pool}) \\ P_{sat}(T) + \sum_{i=4}^N \frac{M_i R_i T}{V_v + \delta V} & (\text{atmosphere}) \end{cases} \quad (2.18)$$

where P_ℓ in Equation (2.7) has been replaced by P_w (the two are equal in this case, and P_v has been replaced by $P_{sat}(T)$, the partial pressure of water vapor in the atmosphere. K is defined in terms of the compressibility of the liquid phase as

$$K = \left(\rho_\ell \frac{\partial P_\ell}{\partial \rho_\ell} \right)^{-1} . \quad (2.19)$$

Equation (2.18) results in a quadratic equation for δV ,

$$(\delta V)^2 + (V_v + KV_\ell \Delta P) \delta V - KV_\ell \sum_{i=4}^N M_i R_i T = 0 , \quad (2.20)$$

where

$$\Delta P = P_w - P_{sat}(T) ; \quad (2.21)$$

and the fact that either V_v or ΔP is zero has been used (the former if the water would be subcooled in the absence of NCGs, the latter if it would be two-phase). If the water is two-phase, the total pressure is best evaluated from the second form of Equation (2.18),

$$P_{tot} = P_w(\rho_w, T) + \sum_{i=4}^N \frac{M_i R_i T}{V_v + \delta V} \quad (2.22)$$

noting that $P_w(\rho_w, T) = P_{sat}(T)$. Otherwise, for pure liquid (saturated or subcooled), the first form of Equation 2.18 gives

$$P_{tot} = P_w(\rho_w, T) + \frac{\delta V}{K V} \quad (2.23)$$

noting that $V_\ell = V$.

At this point, the new atmosphere volume, V_n , is greater than the volume of water vapor from the water equation of state, V_v , by an amount δV (Equation (2.17)). Therefore, in order to maintain the density of water vapor in the atmosphere as $\rho_{v,sat}(T)$, a mass of water equal to $\rho_{v,sat}(T)\delta V$ is transferred from the liquid to the vapor state by simply modifying the quality of water in the volume to be

$$x' = x + \frac{\rho_{v,sat}(T)\delta V}{M_w} \quad (2.24)$$

The mass involved is an extremely small fraction of the liquid mass because δV is much smaller than V_ℓ (liquid water is almost incompressible), and $\rho_{v,sat}(T)$ is much smaller than $\rho_{\ell,sat}(T)$. The energy implications of assigning vapor energy rather than liquid energy to this mass are also very small, and are dealt with by the final adjustment to internal energy described below.

Just as V_n is greater than V_v , the remaining liquid volume is *less* than the value V_ℓ used in the water equation of state. In addition to the correction to the liquid enthalpy given by Equation (2.9), a correction is made to the liquid density. As discussed in conjunction with Equation (2.9), the effect on liquid internal energy is small, and has been ignored. Because the uncorrected value has been used consistently, there are no implications with respect to conservation of energy.

The solution is now complete. A temperature has been found such that the known total internal energy is matched *within the convergence tolerance of the iterative solution procedure*. The pressure and all other thermodynamic properties have been evaluated consistently using that temperature and the known volume and masses. Because the total internal energy is the primary—and conserved—quantity, a final adjustment is made to the

calculated specific internal energies so that Equation (2.10) is satisfied exactly. The adjustment is made either to the water or to the NCGs, depending of which has the greater total heat capacity.

2.3 Required Derivatives

A number of derivatives of the total pressure are required for the implicit solution of the flow equation (see the CVH/FL Reference Manual) or, as will be shown in a later section, for use in solving the nonequilibrium thermodynamic relations in volumes which employ that option. The natural variables for these derivatives are the total energy in the volume, E , the vector of masses in the volume, M , and the available hydrodynamic volume, V . The required derivatives are $(\partial P / \partial E)_{M,V}$, $(\partial P / \partial M_w)_{E,V}$, $(\partial P / \partial M_i)_{E,V}$ [where $4 \leq i \leq N$ denotes the NCGs], and $(\partial P / \partial V)_{E,M}$. Evaluation of these derivatives is straightforward but tedious. The required expressions are presented in Appendix A.

2.4 Partition of Liquid Water between Pool and Atmosphere

Preceding discussions describe a mixed-material equation of state in which it is assumed that water vapor and noncondensable gases (if both are present) are mixed within a common (sub)volume. For a volume in which nonequilibrium thermodynamics is specified, this equation of state will be applied to the pool and atmosphere separately as described in Section 3. Separate mass inventories are calculated for the pool and the atmosphere, and the pool is assumed to contain no noncondensable gases. Therefore, water vapor in the pool is unambiguously interpreted as vapor bubbles (*void*) and liquid water in the atmosphere as vapor droplets (*fog*).

For a volume in which equilibrium thermodynamics is specified, and the equation of state is applied to the entire contents of the volume, the situation is not so simple. The reason is that heat and mass transfer between pool and atmosphere are implicitly included. Therefore, only the total water content and the total energy of the control volume are known, and not the energies and water contents of pool and atmosphere individually.

As stated in the introduction, a basic assumption of the model is that the pool contains water only. If NCGs are present in an equilibrium volume, any liquid water must be subcooled as a consequence of the additional partial pressures of the NCGs. The pool—which can contain no NCGs—can therefore contain no bubbles. In the absence of NCGs, there is no such restriction but, to avoid introduction of an unacceptable discontinuity between the two cases, the equilibrium model assumes that there is no void in the pool.

There is no such thermodynamic basis for defining the partition of liquid water between pool and fog. Both consist of subcooled (in the presence of NCGs) or saturated (in their absence) liquid water. As currently coded, the equilibrium model also assumes that there

is preferential evaporation of, or condensation to, fog, so that the mass of water in the atmosphere is conserved if possible. That is, the new fog mass is calculated as

$$M_{fog}^{new} = \max(M_{fog}^{old} + M_{vap}^{old} - M_{vap}^{new}, 0) \quad . \quad (2.25)$$

and any remaining mass of liquid water (as calculated by the equilibrium equation of state) is assigned to the pool.

3. Nonequilibrium Thermodynamics

As discussed in Section 1, the implementation of nonequilibrium thermodynamics in MELCOR is more restrictive than in some other codes. The underlying equation of state is strictly equilibrium, and does not allow subcooled vapor or superheated liquid. However, if the nonequilibrium option is selected, the pool and atmosphere within a control volume (which are also the two fields in the hydrodynamic equations) are not required to be in thermal or evaporative equilibrium.

3.1 Governing Assumptions

Nonequilibrium thermodynamics assumes that the pool and the atmosphere have equal pressures but that their temperatures may be unequal. As currently implemented, it assumes that all NCGs are in the atmosphere. The pool may contain some water vapor as well as liquid, and the atmosphere may contain some liquid water (*fog*) in addition to vapor. For each field, the total *water* is determined by the mass inventory; the liquid/vapor state is determined implicitly by the energy content.

Given the total volume, the start-of-timestep subvolumes of the pool and of the atmosphere, the total internal energies of the pool and of the atmosphere at these start-of-timestep subvolumes, the mass of water in the pool, and the masses of water and NCGs in the atmosphere, the problem is to calculate the new subvolumes of the pool and of the atmosphere, the temperatures of each, and the common pressure. In computing the subvolumes, it is assumed that the boundary between pool and atmosphere is adiabatic because all heat and mass transfer has already been calculated in the CVH package. However the work done by displacement of the interface has not yet been calculated, and must be included in CVT. It is for this reason that the start-of-timestep subvolumes are needed.

The general equilibrium model described above for volumes in which equilibrium thermodynamics is specified is used to determine the properties of the atmosphere. It may be seen that the same three cases listed in Section 2.1 for equilibrium thermodynamics may occur:

- (1) The atmosphere may contain liquid only (only if there are no NCGs),
- (2) It may contain no liquid, and
- (3) It may contain water vapor and/or NCGs in addition to liquid.

The first case, of course, has no physical significance because an “atmosphere” containing liquid water only is indistinguishable from “pool”. It is included for completeness and then dealt with outside of the CVT package.

Because of the assumption that there are no NCGs in the pool, it could be treated by using the equation of state for water alone. However, in the interest of consistency, the same general equilibrium model is also used to determine its properties. This will also simplify changes to allow NCGs in the pool if desired in future versions of MELCOR.

3.2 Governing Equations

If a volume is to be treated in the nonequilibrium approximation, the pool and the atmosphere are each described by equilibrium thermodynamics. If we consider the pressure to be a function of masses, energy, and volume, and denoted by $P_{equil}(M, E, V)$ the function defined by the treatment of equilibrium thermodynamics in Section 2.2, the problem is to partition the total volume, V , into two components V_p and V_a such that

$$V_p + V_a = V \quad (3.1)$$

and

$$\begin{aligned} & P_{equil} [M_p, E_p + P^{old} (V_p^{old} - V_p), V_p] \\ &= P_{equil} [M_a, E_a + P^{old} (V_a^{old} - V_a), V_a] \end{aligned} \quad (3.2)$$

Here the superscript “old” refers to the value at the start of the timestep. The terms in Equation (3.2) use the old pressure and the change in volume during the timestep to represent the volume work done by the pool on the atmosphere and vice versa. The old pressure (rather than some average over the timestep) must be used for consistency because, for the solution scheme used in the CVH package, mass moved through the flow paths carries *old* enthalpies, and therefore does work with *old* pressures. For example, in an extreme case where all but an insignificant amount of the atmosphere leaves a control volume during a timestep, it will transport an energy of $M_a^{old} h_a^{old}$ in the limit as the remaining mass of the atmosphere goes to zero, consisting of its internal energy plus the volume

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work done by its motion. This will leave the remaining atmosphere with an energy approaching $-P^{old}V_a^{old}$ before the work done on it by the pool is accounted for in CVT. Its new volume and new energy as determined by CVT must also go to zero, which can only happen if the old pressure is used in the volume work term.

Equation (3.2) is solved iteratively, subject to the constraint of Equation (3.1), by using Newton's method with a secant (and ultimately a bisection) backup. In order to avoid roundoff problems, the smaller of V_p and V_a is treated as the primary variable within the iteration. The same model used for equilibrium thermodynamics is used to evaluate P_{equil} and its derivatives for the pool and for the atmosphere subvolumes. Because no heat transfer is included in CVT, the constant entropy (S) (adiabatic) derivatives of pressure with respect to volume

$$\left(\frac{\partial P}{\partial V}\right)_{S,M} = \left(\frac{\partial P}{\partial V}\right)_{E,M} - P \left(\frac{\partial P}{\partial E}\right)_{M,V} \quad (3.3)$$

for the pool and for the atmosphere are used in the Newton iteration. This is consistent with inclusion of the PdV terms in Equation (3.2) [note that $(\partial E / \partial V)_{S,M} = -P$].

3.3 Required Derivatives

Once Equation (3.2) has been solved to determine the volumes V_p and V_a , the derivatives required for solution of the flow equation are easily found from those already available for the subvolumes alone. For a differential change in some variable (mass, energy, or volume) for the pool or for the atmosphere, the differential change in pressure (under the current nonequilibrium assumptions) may be found by simultaneous solution of

$$\begin{aligned} dP_p = & \left(\frac{\partial P_p}{\partial E_p}\right)_{M_p, V_p} (dE_p - PdV_p) + \left(\frac{\partial P_p}{\partial M_{w,p}}\right)_{E_p, V_p} dM_{w,p} \\ & + \sum_{i=4}^N \left(\frac{\partial P_p}{\partial M_{i,p}}\right)_{E_p, V_p} dM_{i,p} + \left(\frac{\partial P_p}{\partial V_p}\right)_{E_p, M_p} dV_p \end{aligned} \quad (3.4)$$

$$\begin{aligned} dP_a = & \left(\frac{\partial P_a}{\partial E_a}\right)_{M_a, V_a} (dE_a - PdV_a) + \left(\frac{\partial P_a}{\partial M_{w,a}}\right)_{E_a, V_a} dM_{w,a} \\ & + \sum_{i=4}^N \left(\frac{\partial P_a}{\partial M_{i,a}}\right)_{E_a, V_a} dM_{i,a} + \left(\frac{\partial P_a}{\partial V_a}\right)_{E_a, M_a} dV_a \end{aligned} \quad (3.5)$$

subject to

$$dP = dP_p = dP_a \quad , \quad (3.6)$$

$$dV_p + dV_a = 0 \quad . \quad (3.7)$$

(The summation over NCGs in the pool is retained in Equation (3.4) to allow future generalization, but the corresponding NCG masses are identically zero under current modeling assumptions.) In these equations P_p and P_a are used to represent P_{equil} (pool) and P_{equil} (atmosphere) and, to avoid further complicating the notation, it has been assumed that a derivative with respect to a component mass is evaluated with all *other* component masses held constant. Note the inclusion of the PdV terms in Equations (3.4) and (3.5); here dE includes only those changes in energy treated by the CVH package, which does not consider volume work done by the pool on the atmosphere of the same calculational volume (or vice versa).

Solution of these equations leads to the desired derivatives. For example, if only dE_p is non-zero, Equations (3.4), (3.5), and (3.6) yield

$$dP = dP_p = \left(\frac{\partial P_p}{\partial E_p} \right)_{M_p, V_p} dE_p + \left[\left(\frac{\partial P_p}{\partial V_p} \right)_{E_p, M_p} - P \left(\frac{\partial P_p}{\partial E_p} \right)_{M_p, V_p} \right] dV_p \quad , \quad (3.8)$$

$$dP = dP_a = \left[\left(\frac{\partial P_a}{\partial V_a} \right)_{E_a, M_a} - P \left(\frac{\partial P_a}{\partial E_a} \right)_{M_a, V_a} \right] dV_a \quad , \quad (3.9)$$

Eliminating dV_p and dV_a by using Equation (3.7), and identifying the adiabatic derivatives defined by Equation (3.3), leads to the result

$$\left(\frac{\partial P}{\partial E_p} \right)_{E_a, M_p, M_a, V} = \frac{\left(\frac{\partial P_a}{\partial V_a} \right)_{S_a, M_a} \left(\frac{\partial P_p}{\partial E_p} \right)_{M_p, V_p}}{\left(\frac{\partial P_a}{\partial V_a} \right)_{S_a, M_a} + \left(\frac{\partial P_p}{\partial V_p} \right)_{S_p, M_p}} \quad . \quad (3.10)$$

The general expressions from which all the required derivatives may be evaluated may be seen to be

$$\left(\frac{\partial P}{\partial \xi_p} \right)_{\{\dots\}} = \frac{\left(\frac{\partial P_a}{\partial V_a} \right)_{S_a, M_a} \left(\frac{\partial P_p}{\partial \xi_p} \right)_{\{\dots\}}}{\left(\frac{\partial P_a}{\partial V_a} \right)_{S_a, M_a} + \left(\frac{\partial P_p}{\partial V_p} \right)_{S_p, M_p}}, \quad (3.11)$$

and

$$\left(\frac{\partial P}{\partial \xi_a} \right)_{\{\dots\}} = \frac{\left(\frac{\partial P_p}{\partial V_p} \right)_{S_p, M_p} \left(\frac{\partial P_a}{\partial \xi_a} \right)_{\{\dots\}}}{\left(\frac{\partial P_a}{\partial V_a} \right)_{S_a, M_a} + \left(\frac{\partial P_p}{\partial V_p} \right)_{S_p, M_p}}. \quad (3.12)$$

where ξ_φ is any one of the variables E_φ , $M_{w,\varphi}$, or $M_{i,\varphi}$, “ φ ” is “ p ” or “ a ”, and $\{\dots\}$ denotes that set of variables which is to be kept constant under variation of ξ_φ .

3.4 Limit of Vanishing Pool or Atmosphere

The separate mass and energy inventories calculated by CVH for the pool and the atmosphere are used to determine the thermodynamic properties of nonequilibrium volumes. In the limit where either the pool or the atmosphere in such a volume becomes extremely small, any loss of precision in calculating the energy content of the vanishing subvolume will have a large effect on the calculated temperature, since its heat capacity goes to zero. Blind application of the model described above leads to unacceptably large excursions in the calculated temperatures of very small pools and atmospheres.

This problem is handled within current coding by switching to the equilibrium formulation whenever a volume specified as nonequilibrium contains only an extremely small (10^{-6}) volume fraction of pool or of atmosphere. One result is that when a nonequilibrium volume becomes completely filled by a two-phase pool, application of the equilibrium model results in an inappropriate separation of the two-phase pool into a pool containing only saturated liquid and an atmosphere containing the saturated water vapor from the bubbles.

This is clearly not a satisfactory solution. The principal problem is that the equilibrium model does not correspond to the infinite mass-and-heat-transfer limit of the nonequilibrium model. However, making the treatment of equilibrium and nonequilibrium

volumes completely consistent would not be trivial, and might require elimination of the assumption that a pool can contain no NCGs.

On the other hand, extending the nonequilibrium model to handle the limit of a vanishing pool or atmosphere would require some modification to constrain the calculated temperature difference between pool and atmosphere. This would almost certainly require inclusion of an implicit contribution to the heat transfer (and possibly the mass transfer) between the pool and the atmosphere, either in CVH or (more likely) within CVT.

4. Other Required Properties

Other thermodynamic properties may be calculated from those returned by the H2O and NCG packages, using familiar thermodynamic relationships.

4.1 Specific Heat at Constant Pressure

The H2O package does not return the specific heat of water at constant pressure. Where this is needed, it is evaluated from the standard relationship

$$c_p = c_v + \frac{T \left(\frac{\partial P}{\partial T} \right)_\rho^2}{\rho^2 \left(\frac{\partial P}{\partial \rho} \right)_T} . \quad (4.1)$$

4.2 Sound Speed

The speed of sound in the pool and that in the atmosphere are calculated by CVT for use in other packages. The speed of sound, C_s , in a material is defined in terms of the adiabatic bulk modulus as

$$C_s^2 = \left(\frac{\partial P}{\partial \rho} \right)_s . \quad (4.2)$$

Through the use of standard thermodynamic manipulations, Equation (4.2) may be recast in the form

$$C_s^2 = \left(\frac{\partial P}{\partial \rho} \right)_T + \frac{T \left(\frac{\partial P}{\partial T} \right)_\rho^2}{\rho^2 c_v} ; \quad (4.3)$$

All of the variables in the latter form are available from the H2O and NCG packages. For a mixture, the sound speed calculated is that given by Equation (4.3) using mixture properties. It corresponds to an equilibrium (long-wavelength) limit, where there is adequate time for energy exchange between species.

Appendix A: Derivatives

This Appendix presents the equations necessary for evaluation of the derivatives of the pressure of an equilibrium mixture with respect to energy, total volume, and various masses. Considerable care has been taken to indicate, using subscripts, what is kept constant in each derivative. When no subscripts are present, the explicit derivative is intended—that is, the derivative in terms of variables appearing explicitly in the definition of the function. However, subscripts are included in some cases where the derivative is, in fact, an explicit one. In order to avoid further complicating the notation, it has been assumed that a derivative with respect to a component mass is evaluated with all *other* component masses held constant.

In the following sections, the pressure is considered to be an explicit function of ρ_w , T , V , and V_n , and of $M_i R_i$ for each NCG. The chain rule will be used in evaluating the desired results. V_n will be treated as an explicit function of T , M_w , and V , and the $M_i R_i$, with derivatives given in Section A.2. V_v will be treated as an explicit function of T , M_w , and V , with derivatives given in Section A.3.

A.1 Derivatives of the Pressure

The various results presented in Equations (2.12), (2.13), (2.22), and (2.23) reduce to only two cases. They are:

- (1) If the water would be single-phase (saturated or subcooled) liquid in the absence of NCGs, the total pressure including the effects of NCG is given by Equation (2.23) (noting that $\delta V = V_n$) as

$$P = P_w(\rho_w, T) + \frac{V_n}{KV} \quad , \quad (A.1)$$

with explicit derivatives

$$\frac{\partial P}{\partial \rho_w} = \frac{\partial P_w}{\partial \rho_w} \quad , \quad (A.2)$$

$$\frac{\partial P}{\partial T} = \frac{\partial P_w}{\partial T} \quad , \quad (A.3)$$

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$$\frac{\partial P}{\partial V} = -\frac{V_n}{KV^2} \quad , \quad (\text{A.4})$$

$$\frac{\partial P}{\partial V_n} = \frac{1}{KV} \quad , \quad (\text{A.5})$$

$$\frac{\partial P}{\partial (M_i R_i)} = 0 \quad . \quad (\text{A.6})$$

(2) In all other cases, the pressure is

$$P = P_w(\rho_w, T) + \sum_{i=4}^N \frac{M_i R_i T}{V_n} \quad , \quad (\text{A.7})$$

with explicit derivatives

$$\frac{\partial P}{\partial \rho_w} = \frac{\partial P_w}{\partial \rho_w} \quad , \quad (\text{A.8})$$

$$\frac{\partial P}{\partial T} = \frac{\partial P_w}{\partial T} + \sum_{i=4}^N \frac{M_i R_i}{V_n} \quad , \quad (\text{A.9})$$

$$\frac{\partial P}{\partial V} = 0 \quad , \quad (\text{A.10})$$

$$\frac{\partial P}{\partial V_n} = -\sum_{i=4}^N \frac{M_i R_i T}{V_n^2} \quad , \quad (\text{A.11})$$

$$\frac{\partial P}{\partial (M_i R_i)} = \frac{T}{V_n} \quad . \quad (\text{A.12})$$

The derivative of pressure with respect to energy is evaluated from

$$\left(\frac{\partial P}{\partial E} \right)_{M,V} = \left(\frac{\partial P}{\partial T} \right)_{M,V} \bigg/ \left(\frac{\partial E}{\partial T} \right)_{M,V} \quad , \quad (\text{A.13})$$

where

$$\left(\frac{\partial P}{\partial T}\right)_{M,V} = \frac{\partial P}{\partial T} + \frac{\partial P}{\partial V_n} \left(\frac{\partial V_n}{\partial T}\right)_{M,V} , \quad (\text{A.14})$$

$$\left(\frac{\partial E}{\partial T}\right)_{M,V} = M_w c_{v,w} + \sum_{i=4}^N M_i c_{v,i} . \quad (\text{A.15})$$

Here, c_v is the specific heat at constant volume, all water properties and their derivatives come from the H2O package, and NCG properties come from the NCG package. Derivatives of V_n will be discussed in Section A.2.

The derivative of pressure with respect to total volume is given by

$$\left(\frac{\partial P}{\partial V}\right)_{E,M} = \frac{\partial P}{\partial V} + \frac{\partial P}{\partial V_n} \left(\frac{\partial V_n}{\partial V}\right)_{T,M} - \frac{\rho_w}{V} \frac{\partial P_w}{\partial \rho_w} + \left(\frac{\partial P}{\partial T}\right)_{M,V} \left(\frac{\partial T}{\partial V}\right)_{E,M} \quad (\text{A.16})$$

Derivation of Equation (A.16) requires multiple application of the chain rule since, for example, V_n is an explicit function of T rather than of E . The additional term is responsible for the appearance of $(\partial P / \partial T)_{M,V}$ (Equation (A.14)) rather than simply $(\partial P / \partial T)$. Finally,

$$\left(\frac{\partial T}{\partial V}\right)_{E,M} = -\left(\frac{\partial E}{\partial V}\right)_{T,M} / \left(\frac{\partial E}{\partial T}\right)_{M,V} , \quad (\text{A.17})$$

in which

$$\left(\frac{\partial E}{\partial V}\right)_{T,M} = -P_w + T \frac{\partial P_w}{\partial T} ; \quad (\text{A.18})$$

derivation of Equation (A.18) requires use of the Maxwell relation $(\partial S / \partial V)_{T,M} = (\partial P / \partial T)_{M,V}$, and only water contributes because the internal energy of an ideal gas is independent of its volume.

The derivative of pressure with respect to water mass is given by

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$$\left(\frac{\partial P}{\partial M_w}\right)_{E,V} = \frac{\partial P}{\partial V_n} \left(\frac{\partial V_n}{\partial M_w}\right)_{T,V} + \frac{1}{V} \frac{\partial P_w}{\partial \rho_w} + \left(\frac{\partial P}{\partial T}\right)_{M,V} \left(\frac{\partial T}{\partial M_w}\right)_{E,V}, \quad (\text{A.19})$$

where

$$\left(\frac{\partial T}{\partial M_w}\right)_{E,V} = - \left(\frac{\partial E}{\partial M_w}\right)_{T,V} / \left(\frac{\partial E}{\partial T}\right)_{M,V}, \quad (\text{A.20})$$

$$\left(\frac{\partial E}{\partial M_w}\right)_{T,V} = e_w(\rho_w, T) - \frac{1}{\rho_w} \left(\frac{\partial E}{\partial V}\right)_{T,M}; \quad (\text{A.21})$$

the relation between $(\partial E / \partial M_w)_{T,V}$ and $(\partial E / \partial V)_{T,M}$ given by Equation (A.18) is easily seen from Equation (2.10).

The derivative of pressure with respect to the mass of the NCG is given by

$$\left(\frac{\partial P}{\partial M_i}\right)_{E,V} = R_i \left(\frac{\partial P}{\partial (M_i R_i)} + \frac{\partial P}{\partial V_n} \frac{\partial V_n}{\partial (M_i R_i)} \right) - \left(\frac{\partial P}{\partial E}\right)_{M,V} \left(\frac{\partial E}{\partial M_i}\right)_{T,V}, \quad (\text{A.22})$$

where

$$\left(\frac{\partial E}{\partial M_i}\right)_{T,V} = e_i(T). \quad (\text{A.23})$$

A.2 Derivatives of the Volume Available to NCG

The equations in the preceding section contain derivatives of the volume available to NCGs, V_n . Unless there are both NCGs and liquid water in the volume, δV is zero, V_n is identical to V_v , and we have

$$\left(\frac{\partial V_n}{\partial V}\right)_{T,M} = \left(\frac{\partial V_v}{\partial V}\right)_{T,M} \quad (\text{no NCG or no liquid}) \quad (\text{A.24})$$

$$\left(\frac{\partial V_n}{\partial T}\right)_{M,V} = \left(\frac{\partial V_v}{\partial T}\right)_{M,V} \quad (\text{no NCG or no liquid}) \quad (\text{A.25})$$

$$\left(\frac{\partial V_n}{\partial M_w}\right)_{T,V} = \left(\frac{\partial V_v}{\partial M_w}\right)_{T,V} \quad (\text{no NCG or no liquid}) \quad (\text{A.26})$$

(Expressions for derivatives of V_v are given in Section A.3.) The derivative with respect to NCG masses is more complicated, and must be found from the general case below.

If δV is non-zero (case 3 of Section 2.2), we form the differential of Equation (2.20), the quadratic defining δV . It may be put in the form

$$(V^* + 2\delta V)dV_n = \left(V^* + \delta V - V_n \frac{\delta V}{V_\ell}\right)dV_v + \left(V_n \frac{\delta V}{V_\ell}\right)dV \\ - KV_\ell \delta V d(\Delta P) + KV_\ell d\left(\sum_{i=4}^N M_i R_i T\right), \quad (\text{A.27})$$

where

$$V^* = V_v + KV_\ell \Delta P, \quad (\text{A.28})$$

through use of Equation (2.20) itself. As noted in the discussion of Equation (2.20), either $V_v = 0$ if the water is subcooled, or $\Delta P = 0$ if it is saturated. The variable V^* is used to simplify the analysis by reducing the number of cases to be considered.

From Equation (A.27), we may identify the following derivatives (noting that the pressure derivatives vanish unless the water is subcooled, in which case $V_\ell = V$):

$$(V^* + 2\delta V)\left(\frac{\partial V_n}{\partial V}\right)_{T,M} = \left(V^* + \delta V - V_n \frac{\delta V}{V_\ell}\right)\left(\frac{\partial V_v}{\partial V}\right)_{T,M} \\ + V_n \frac{\delta V}{V_\ell} + K \delta V \rho_w \frac{\partial P_w}{\partial \rho_w} \quad (\text{A.29})$$

$$(V^* + 2\delta V)\left(\frac{\partial V_n}{\partial T}\right)_{M,V} = \left(V^* + \delta V - V_n \frac{\delta V}{V_\ell}\right)\left(\frac{\partial V_v}{\partial T}\right)_{M,V} \\ + KV_\ell \left[\delta V \left(\frac{dP_{sat}}{dT} - \frac{\partial P_w}{\partial T}\right) + \sum_{i=4}^N M_i R_i\right] \quad (\text{A.30})$$

$$(V^* + 2\delta V) \left(\frac{\partial V_n}{\partial M_w} \right)_{T,V} = \left(V^* + \delta V - V_n \frac{\delta V}{V_\ell} \right) \left(\frac{\partial V_v}{\partial M_w} \right)_{T,V} - K \delta V \frac{\partial P_w}{\partial \rho_w} \quad (\text{A.31})$$

and

$$(V^* + 2\delta V) \left[\frac{\partial V_n}{\partial (M_i R_i)} \right]_{T,V} = K V_\ell T \quad (\text{A.32})$$

Unless there are both NCGs and liquid water, Equations (A.29), (A.30), and (A.31) reduce to Equations (A.24), (A.25), and (A.26), respectively.

If there are no NCGs, the derivative of pressure with respect to NCG mass, given by Equation (A.32), reduces to

$$\left[\frac{\partial V_n}{\partial (M_i R_i)} \right]_{T,V} = \frac{K V_\ell T}{V^*} \quad (\text{no NCG}) \quad (\text{A.33})$$

a result which could not have been obtained from the results derived in the absence of NCGs. Some care must be taken in evaluating Equation (A.33) in the case of saturated liquid. Whether this situation is approached from the subcooled side ($V_v = 0, P \rightarrow 0+$) or from the two-phase side ($\Delta P = 0, V_v \rightarrow 0+$), the denominator V^* goes to 0.

Ideally, one should maintain consistency regardless of how this state of saturated liquid water and no NCG is approached, taking into account that it may involve either case 1 or case 2 in Section A.1. The current coding simply prevents the division by zero. This simple approach has not been found to cause any problems in practice.

A.3 Derivatives of the Vapor Volume

The equations in the preceding section contain derivatives of the volume which would be occupied by water vapor in the absence of NCG with respect to total volume, temperature, and water mass. There are three cases to be considered:

- (1) If there is no liquid (no water, or vapor only), $V_v = V$ and

$$\left(\frac{\partial V_v}{\partial V}\right)_{T, M_w} = 1 \quad (\text{A.34})$$

$$\left(\frac{\partial V_v}{\partial T}\right)_{M_w, V} = 0 \quad , \quad (\text{A.35})$$

$$\left(\frac{\partial V_v}{\partial M_w}\right)_{T, V} = 0 \quad . \quad (\text{A.36})$$

(2) If there is water but no vapor (liquid only), $V_v = 0$, and

$$\left(\frac{\partial V_v}{\partial V}\right)_{T, M_w} = 0 \quad , \quad (\text{A.37})$$

$$\left(\frac{\partial V_v}{\partial T}\right)_{M_w, V} = 0 \quad , \quad (\text{A.38})$$

$$\left(\frac{\partial V_v}{\partial M_w}\right)_{T, V} = 0 \quad . \quad (\text{A.39})$$

Otherwise (two-phase water), V_v is given by the primary form of Equation (2.15) (not the bounds), and the derivatives are

$$\left(\frac{\partial V_v}{\partial V}\right)_{T, M_w} = \frac{\rho_{\ell, sat}}{\rho_{\ell, sat} - \rho_{v, sat}} \quad , \quad (\text{A.40})$$

$$\left(\frac{\partial V_v}{\partial T}\right)_{M_w, V} = \frac{V_{\ell} \frac{d\rho_{\ell, sat}}{dT} + V_v \frac{d\rho_{v, sat}}{dT}}{\rho_{\ell, sat} - \rho_{v, sat}} \quad , \quad (\text{A.41})$$

$$\left(\frac{\partial V_v}{\partial M_w}\right)_{T, V} = -\frac{1}{\rho_{\ell, sat} - \rho_{v, sat}} \quad . \quad (\text{A.42})$$

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The total derivatives of saturation densities with respect to temperature are, of course, to be taken along the phase boundaries. They are evaluated from tables included in the H₂O package.